The Heterogeneous Chemistry of Acetone and Methanol in Sulfuric Acid Solutions: Implications for the Upper Troposphere

Sean M. Kane, Raimo S. Timonen, and Ming-Taun Leu
Earth and Space Sciences Division, Jet Propulsion Laboratory,
California Institute of Technology, Pasadena, CA 91109

Abstract

The uptake of acetone vapor by liquid sulfuric acid has been investigated over the range of 40-87 wt. % H_2SO_4 and between the temperatures of 198 to 300 K. Studies were performed with a flow-tube reactor, using a quadrupole mass spectrometer for detection. At most concentrations studied (40 to 75 wt. %), acetone was physically absorbed by sulfuric acid without undergoing irreversible reaction. However, at acid concentrations at or above 80-wt. %, reactive uptake of acetone was observed, leading to products such as mesityl oxide and/or mesitylene. From time-dependent uptake data and liquid-phase diffusion coefficients calculated from molecular viscosity, the effective Henry's law solubility constant (H*) was determined. The solubility of acetone in liquid sulfuric acid was found to increase with increasing acid concentration and decreasing temperature. In the 75 wt. % and 230 K range, the value for H* was found to be ~ $2x10^6$ M/atm. This value suggests that acetone primarily remains in the gas phase rather than absorbing into sulfate aerosols under atmospheric conditions.

The uptake of gas-phase methanol by liquid sulfuric acid has also been investigated over the composition range of 40 - 85 wt % H_2SO_4 and between the temperatures of 210 - 235 K. While reversible uptake was the primary mechanism at low acid concentrations, irreversible reaction between methanol and sulfuric acid at low temperatures, forming methyl hydrogen sulfate and dimethylsulfate, was observed at all

concentrations. Above 65 wt % H_2SO_4, more than 90 % of uptake was found to be reactive. On the basis of the uptake data and the calculated liquid-phase diffusion coefficients, the product of the effective Henry's law constant (H*) and the square root of the overall liquid-phase reaction rate (k_l) was calculated as a function of acid concentration and temperature. Implications to atmospheric chemistry in the upper troposphere are briefly discussed.